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DETROIT

A Rapid Quantitative Analysis of Collagen

A METHOD for measuring the amino acid content of collagen in a relatively short time and using simple apparatus has been developed by the National Bureau of Standards leather laboratory.[1] The procedure, an application of two-dimensional paper chromatography, was worked out by James M. Cassel by modifying and adapting a recently published qualitative method.[2] The quantitative technique can be applied not only to collagen, the parent substance of leather, but also to the derivatives and degradation products of collagen. In contrast to other methods currently employed, it enables the analyst to follow with a high degree of detail the reactions and changes in which collagen may be involved. It is therefore expected to provide a useful tool in understanding the structure of collagen and the properties of leather.

Improvements in technique during the last few decades have made chromatography one of the more important methods available to the analytical chemist. The partition chromatographic process brings about separation of components in a mixture by distributing the solutes between two liquid phases, one of which is mobile and the other essentially fixed by sorption to a support, i. e., to a column of silica gel or to a sheet of cellulose paper. In one form of the method, a small quantity of unknown mixture is applied to one end of a strip of paper and that end placed in an appropriate irrigating solution. The solution rises by capillary action and carries the mixture with it. Mainly because of differences in solubility, however, the various components move up the support medium at different rates. After a period of time, the components are spread out into a series of separate patches.

The use of paper as the chromatographic adsorbent has broadened the range of application of the method, and at the same time, has made it accessible to even the most modestly equipped laboratories. The use of paper also facilitates two-dimensional chromatography. If a drop of unknown mixture is applied to a corner of a paper square and solution is passed through the paper parallel to one of the edges, the unknown will spread out into a line of patches along one edge of the square. Often, however, the separation is not complete, some of the patches being still made up of several components. If now another solvent is passed through the paper perpendicularly to the line of patches, each of the latter may be split up into several patches, the final result being a two-dimensional pattern of patches on the paper.

The Bureau's method produces separation of all 18 of the amino acids of collagen, with the exception that lysine and hydroxylysine are separated as a single entity, as are also leucine and isoleucine. The procedure is simple and requires for accurate analysis as little as 150 mg of protein per chromatogram. If certain precautions are observed, very good reproducibility of data is obtained.

The first step in the procedure is to apply, by micropipet, a small spot of the solution to be analyzed to the corner of a sheet of Whatman No. 1 paper, 37 cm square. The sheet is then stapled in the form of a cylinder and placed spot downward in a glass cylinder, 6 in. in diameter and 12 in. high, containing the solvent mixture. A crystallizing dish is inverted and

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This simple equipment is used in quantitative analysis of amino acids in collagen, the principal constituent of leather. A drop of unknown mixture is placed in corner of chromatographic paper square. Chemist, as shown, puts paper into a glass cylinder with irrigating solution at bottom. At left, glass cylinder is covered with a crystallizing dish sealed on with electrical tape. Later, paper is rerolled at right angles to original direction and put into another irrigating solution. Final result is chromatogram, center, showing each component as separate patch.

sealed to the top of the chamber with electrical tape to serve as a tight sealing lid.

The paper is irrigated in the first direction with a mixture of methyl alcohol, water, and pyridine. After this, it is removed, dried, restapled, and then irrigated in the second direction with tertiary butanol, water, and diethylamine. Once again the sheet is dried, and the last traces of diethylamine are removed by hanging the sheet in a steam hood at 75° C for approximately 7 min. An alcohol solution of the coloring agent, ninhydrin, is sprayed on the sheet, and the color is developed under carefully chosen conditions of temperature and humidity.

At this point the chromatographic separation of the amino acid components, with the exceptions noted, is complete, each component appearing as an irregular, colored patch on the paper. Each of the spots is now cut out and sliced into small strips. The strips, in turn, are placed in test tubes and washed out with fixed quantities of aqueous *n*-propanol. Optical densities are then read with a spectrophotometer set at 570 mμ for all components except proline and hydroxyproline, which are read at 350 mμ. Finally, the amount of each amino acid present is determined by comparing the optical densities with calibration curves obtained from standard solutions run in the same manner.

Amino acid values for collagen as determined by this technique agree well with those reported in the literature. If 4 to 8 chromatograms are run per sample, quantitative information concerning all the amino acids in either collagen, a collagen derivative, or a collagen degradation product can be obtained in only 4 or 5 days. If conditions are maintained constant throughout the procedure, standards need not be run simultaneously with the unknowns and hence an important saving in labor and time is achieved.

The development of a rapid quantitative analysis for collagen is part of a larger program of research that the Bureau is conducting on the physical constants and structure of leather. Basic information on leather and collagen, the principal constituent of cattle hide, is needed to assure continued advancement in methods of tanning and leather manufacture. Related investigations now in progress deal with the pore structure of the leather matrix, specific heats of collagen and leather, and the effects of high pressure. The Bureau's method for analyzing collagen is being applied to a study of the reaction of collagen with nitrous acid. It is also planned to use the new technique to obtain information about the layerwise distribution of amino acids in hides and the effect on the distribution produced by various types of degradation processes.

[1] *For further technical details, see* A paper chromatographic analysis for collagen and collagen derivatives, *by James M. Cassel, J. Am. Leather Chemists' Assoc. (in press).*

[2] Two-dimensional paper chromatographic system with high resolving power for amino acids, *by R. Redfield, Biochim. et Biophys. Acta* **10**, 344 (1953).

The first description of paper chromatographic methods for the analysis of protein hydrolysates was given in 1944 by Consden, Gordon, and Martin.

Preferred Circuits Handbook

THE MANUAL entitled *Handbook Preferred Circuits, Navy Aeronautical Equipment*, NAVAER 16-1-519, by J. H. Muncy ($1.75), is now available from the Government Printing Office, Washington 25, D. C.

This one-volume, looseleaf handbook,[1] made available by NBS and the Navy Bureau of Aeronautics, is composed of two parts, (1) the Preferred Circuits Manual and (2) Notes to the Preferred Circuits Manual. The manual presents 32 preferred circuits, including voltage regulators, multivibrators, blocking oscillators, video detectors, and amplifiers. Schematics of each circuit are provided, together with characteristics and other information, permitting ready selection and construction; successive pages explain use and design methods. The preferred circuits were derived after experimental measurements had been made on a large number of examples taken from both commercial and military electronic equipment. The notes explain the steps that led to the selection and design of each preferred circuit, and will be of especial value to either the experienced or inexperienced de-

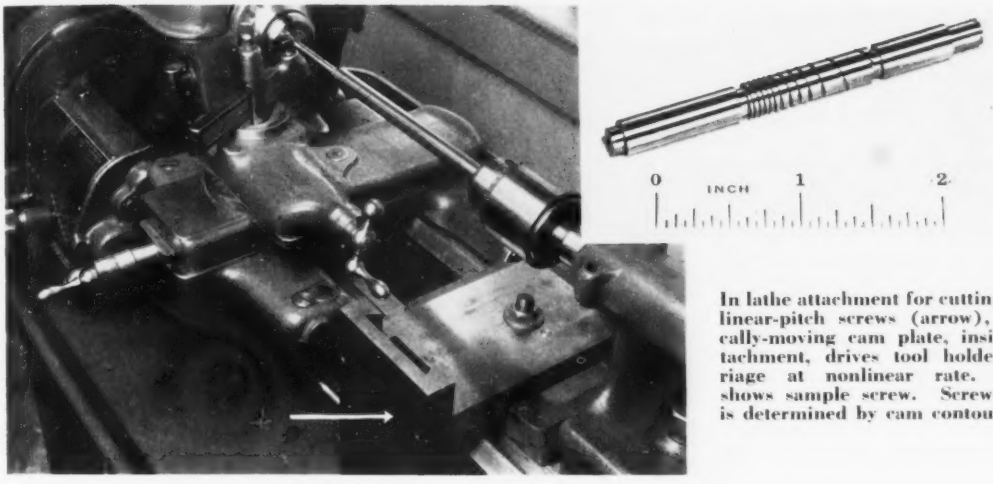
signer whose interest extends beyond an immediate problem.

The handbook has been formally published for wide distribution to promote the standardization of electronic circuits. Its main purpose is to encourage voluntary reduction of unnecessary circuit variations in military equipment. If standardization of electronic circuits is achieved, even in part, substantial economies will be realized. For the manufacturer, standardization will result in lower production costs, quicker shifting from development to production, lower parts inventories, simplification of mechanized production, and conservation of engineering manpower. For the military services, standardization will result in lower procurement costs, simpler maintenance training, shorter lead time on delivery of equipment, fewer spare parts at field installations, and greater operational reliability.

Supplements to the Handbook Preferred Circuits will be issued from time to time and may be purchased from the Government Printing Office. As the supplements become available, announcement will be made.

[1] *A more complete summary of this program appeared in NBS Tech. News Bull.* **39**, *134 (October 1955).*

Lathe Attachment for Cutting Nonlinear-Pitch Screws



In lathe attachment for cutting nonlinear-pitch screws (arrow), vertically-moving cam plate, inside attachment, drives tool holder carriage at nonlinear rate. Insert shows sample screw. Screw pitch is determined by cam contour.

A SIMPLE lathe attachment has been developed that will cut screw threads with a nonlinear pitch. The device consists essentially of a vertically-moving cam plate that bears against the tool holder carriage and moves the carriage horizontally. The attachment is primarily for cutting threads on drive screws of permeability-tuned rf inductors, but could be used to provide screws wherever a fixed, nonlinear function generator is required in electromechanical equipment. The device was designed by G. Shapiro and R. O. Stone of the engineering electronics laboratory for a Navy Bureau of Aeronautics-sponsored program of radio receiver subminiaturization.

In the development of an inductively tuned subminiaturized receiver, design considerations required the tuning dial to be as linear as possible for maximum reading ease. To achieve such a linear presentation, it was necessary in this case that the tuning inductor be wound uniformly and the slug displaced nonuniformly. The simplest and least space-consuming mechanism for achieving nonlinear slug displacement is a screw with a nonlinear pitch. If the cam curve of the lathe attachment is shaped correctly, the resulting screw thread makes it possible to achieve a frequency response directly proportional to screw rotation with a conventional tuning slug in a conventional inductor.

The nonlinear screw-cutting device can be attached to a standard lathe. The lathe is not altered in any way, although it is often desirable to remove the apron before the attachment is locked rigidly to the bed. The attachment contains a sliding cam plate, constrained to move only in a vertical direction. It is driven up and down by engaging a rack to a pinion gear keyed to the lead screw of the lathe. The cam contour cut on the side of the cam plate moves upward at a constant rate, bears against the tool-holder carriage, and displaces the carriage sideways. The cam contour controls the nonlinear motion of the carriage.

The cam contour is easily established from (1) the curve of frequency versus slug penetration into the inductor, (2) the vertical length of the cam, and (3) the horizontal cam dimension.

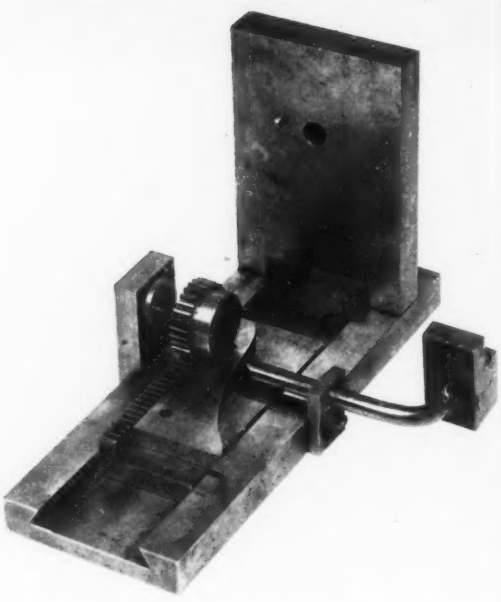
To find the frequency-displacement curve, the inductor and its tuning slug are placed in a jig containing a conventional linear screw drive for the slug. The inductor is resonated with the appropriate capacitance

When attachment is in place on lathe, pinion gear is keyed to lead screw and drives rack fastened to cam plate. Curve of cam plate displaces round bar and block transmitting nonlinear motion to tool holder carriage.

in a Q-meter. Readings are taken of the resonant frequency at incremental values of slug penetration into the inductor. The resulting curve, properly scaled, provides the shape of the variable contour.

The maximum vertical dimension of the cam is limited by the vertical travel of the cam attachment. The useful portion of the contour is selected at about 90 percent of the total travel. Two arbitrarily shaped cam sections, one on each end of the useful portion of the curve, are added to provide time to allow the lathe operator to back out his cutting tool and to reverse the lathe. As the threads cut by these end sections are never engaged in the tuner, their outlines are not important.

The number of revolutions the nonlinear screw must make to displace the slug over its entire tuning range is chosen by the designer. The gear ratio between the headstock spindle and the lead screw is set to a value that will displace the sliding cam plate about 90 percent of its maximum possible vertical travel for the desired number of revolutions of the screw blank. This vertical distance is then divided into as many equal increments of length as there are increments of frequency for which slug displacements have been plotted. The horizontal component of the contour is, of course, determined from the length of the screw to be cut. The horizontal and vertical coordinates, appropriately scaled to the dimension of the cam, are then plotted on the cam blank. As soon as the contour is machined, the cam plate is fastened to the attachment, where it is ready to guide the carriage in cutting the thread.



If a straight, pivoted bar is used in place of the cam in this attachment, it becomes another useful laboratory tool. By adjusting the slope of the bar and clamping it in place at the appropriate angle, it becomes a cam surface that permits the cutting of any nonstandard linear screw thread for which gear ratios in the lathe are not available.

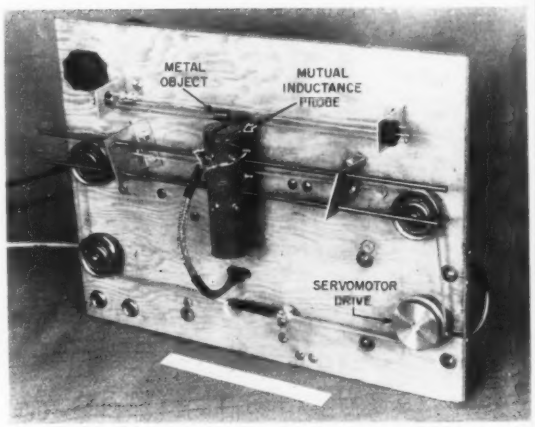
For further technical details, see Subminiaturization techniques for low frequency receivers, *NBS Circular 545, 80.50, available from Superintendent of Documents, Government Printing Office, Washington 25, D. C.*

An Electronic Position-Tracking Instrument

THE electronic instrumentation laboratory has developed an electronic tracking device that automatically follows the position of a metallic object inside an enclosure of nonconducting material. The probe containing the coils of a mutual inductance transducer detects the motion of the object without direct physical contact.

The tracking system makes use of the variation in the mutual inductance between the coils as the position of a nearby electrically-conducting object changes.[1] The signals from the mutual inductance coils control a servomechanism that makes the probe follow the movements of the metallic object. The proximity tracking device, developed by L. A. Marzetta, can be applied to the tracking of the metallic bead inside a rotameter flow tube for remote indication or the detecting of mechanical motion where access is limited.

The mutual inductance transducer was first used at the Bureau in the development of an electronic micrometer.[2] Its principle has since been adapted to a number of other noncontacting displacement gages



This electronic tracking device automatically follows metallic object inside glass tubing without direct physical contact.

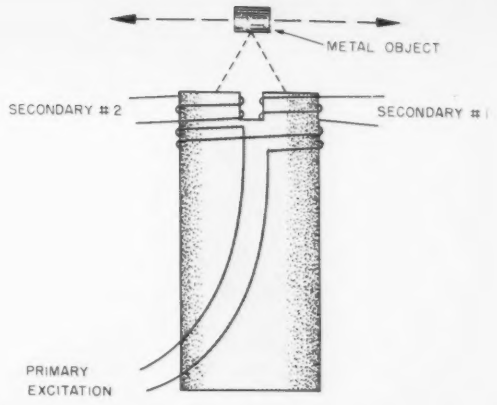
Signals from the mutual inductance coils control servomechanism that makes probe follow movements of metallic object.

for both static and vibratory types of measurements.[3] A typical mutual inductance probe usually contains two coplanar, coaxial coils wound on a dielectric core. An rf source that is regulated with respect to the product of the frequency and current energizes the primary coil. The a-c voltage induced in the secondary then depends on the distance from the probe to a nearby, electrically-conducting reference plate. Suitable electronic circuitry detects and amplifies the output voltage from the secondary coil, and this voltage is indicated on a calibrated meter that gives the change in probe-to-surface measurements in inches or centimeters. Although the tracking instrument is intended only as a position-sensing device, it operates on the same principle as the mutual inductance measuring gages.

The position tracker detects either magnetic or nonmagnetic electrically-conducting materials. The object may be a small, pea-size piece of solid material or a hollow body having a wall thickness of less than 0.001 in. Smaller objects can be tracked, but at less separation or with a more sensitive system. With the Bureau's instrument, an object can be detected and followed at a distance of 0.5 in.; the dead zone of detectable motion is 0.005 in. If the object is long with respect to its width, it will be tracked with the centerline of the probe bisecting the object. The probe can "see" the metallic object through air, glass, water, vacuum, or any opaque dielectric medium equally well. A slight repulsive force is exerted on the metallic object by the induced eddy currents—about 10 mg with the level of current excitation used.

An rf oscillator excites the primary winding of the probe. The frequency for this particular application is 1.5 Mc. Another frequency could be chosen provided that the operating regions of instability are avoided. The self-resonant frequency of each of the windings, together with their lead capacities, should be 2 to 5 times higher than the excitation frequency.

Unlike the usual mutual inductance probe that has but one secondary, the tracking instrument has two secondaries. The two are necessary to determine the direction in which the object moves. The induced voltages in the secondary coils are equal only when the object is equidistant from the two coils. If the object moves to one side or the other, the two voltages are different. It is this difference that develops the servo-control signal corresponding to the object's position.

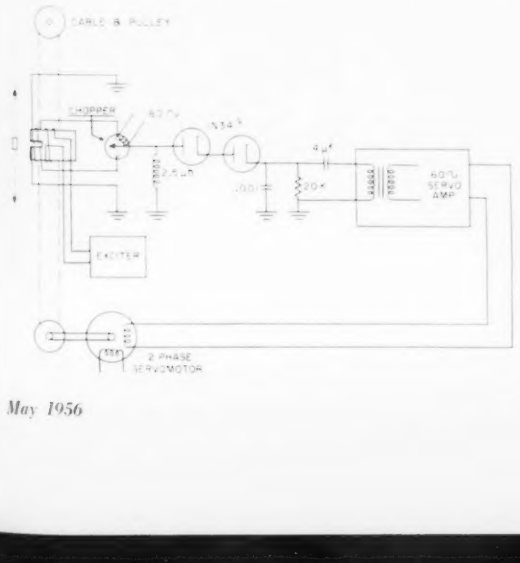


The output voltages from the two secondaries are alternately sampled by a 60-cycle chopper relay and detected to remove the rf carrier. The amplitude of the signal is a measure of the voltage difference between the two coils; the phase polarity depends on which coil has the larger signal. Thus, the position of the object determines the phase of the control signal. The control signal is amplified and applied to one winding of a servomotor that has two windings in quadrature; the second winding is energized by the same 60-cycle power source that supplies power to the chopper relay that samples the control signal. Signal phase and amplitude determine motor direction and speed. The motor is coupled to the probe and repositions it in the direction in which the object moves. The null repositioning voltage is achieved when the centerline of the probe bisects the metallic object; the signals from the secondaries are then very nearly equal.

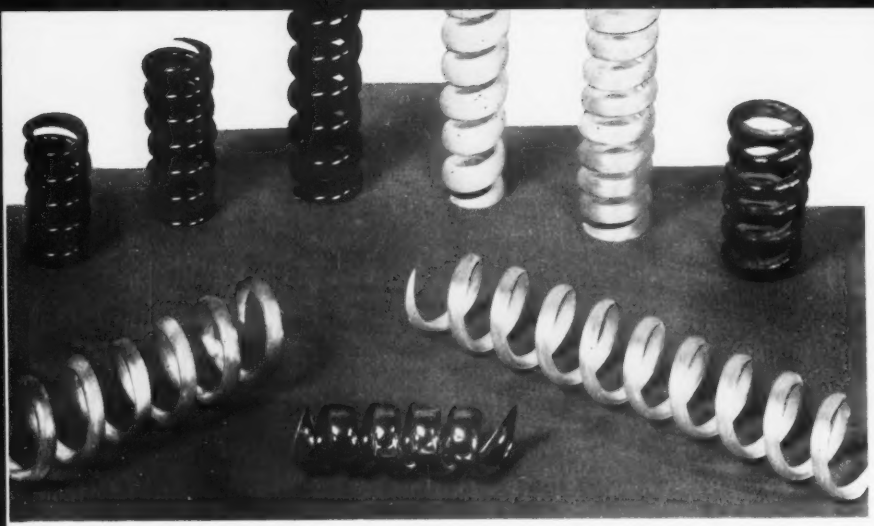
[1] Eddy-current mutual inductance transducers with high-conductivity reference plates, *by H. M. Joseph and N. Newman, AIEE Paper No. 55-4, Communications and Electronics Transactions (March 1955).*

[2] Technical details of an electronic micrometer, *Electronics* **20,** *11 (November 1947).*

[3] Electronic micrometer, *NBS Tech. News Bull.* **31,** *37 (April 1947)*; Micromanometer, *NBS Tech. News Bull.* **34,** *137 (October 1950)*; Oil film thickness indicator, *NBS Tech. News Bull.* **35,** *120 (August 1951)*; Electronic sensing of mercury column height, *NBS Tech. News Bull.* **35,** *26 (February 1952)*; Vibration pickup calibrator, *NBS Tech. News Bull.* **37,** *181 (December 1953)*; A shaft displacement indicator, *NBS Tech. News Bull.* **38,** *70 (May 1954)*; Design criteria for mutual-inductance transducers, *NBS Tech. News Bull.* **39,** *36 (March 1955).*



In position-tracking instrument, exciter (rf oscillator) energizes primary probe winding. Signals from secondaries are sampled by chopper, detected, amplified, and fed to servomotor winding. Amplitude and phase relations of signal determine speed and direction in which servomotor moves probe.



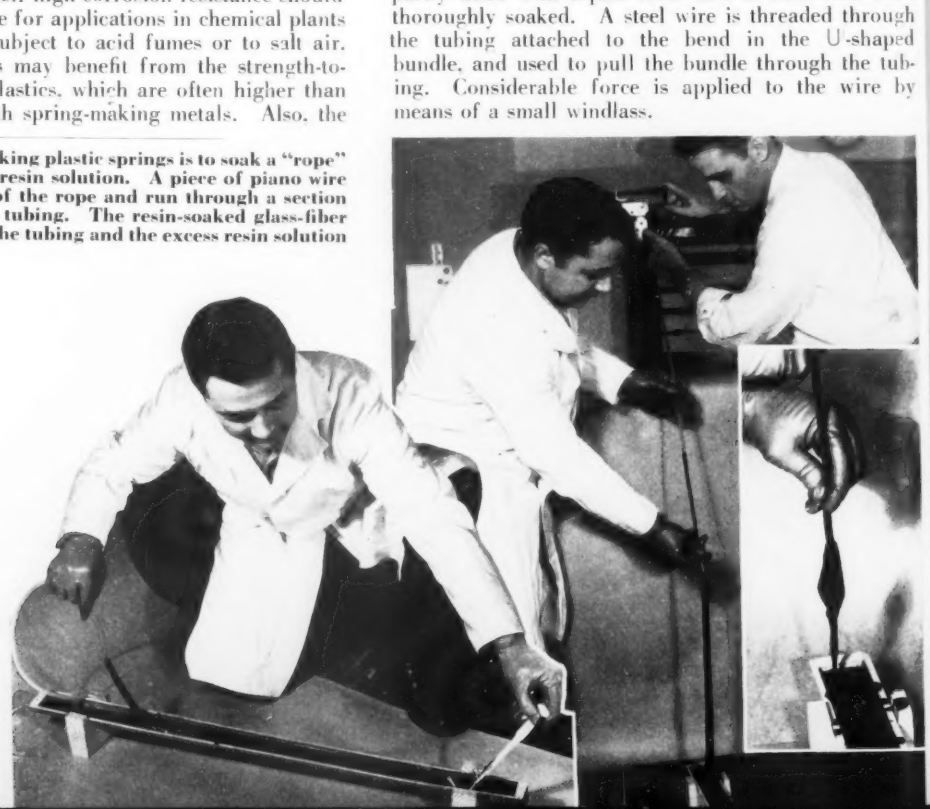
Plastic Springs

A PRACTICAL procedure for mass-producing plastic springs has been developed by the National Bureau of Standards in work sponsored by the Army Ordnance Corps. Springs formed in this way [1] from glass fiber-reinforced resin have desirable mechanical properties for a wide range of applications. Until now, there have been no suitable techniques for making plastic springs of the types needed.

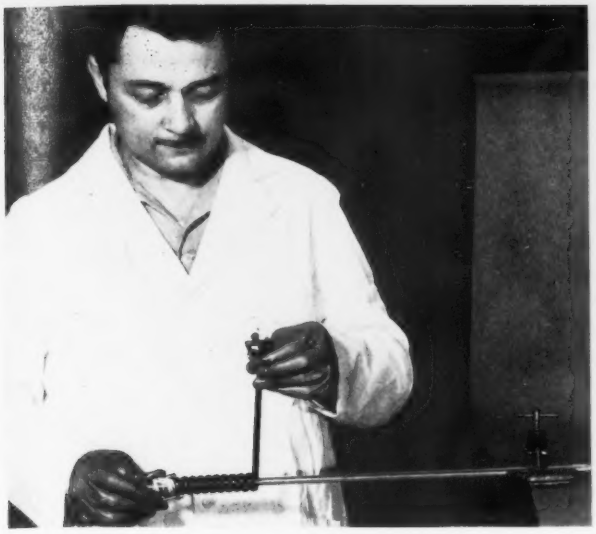
Polymeric materials, such as plastics and rubbers, have a number of inherent advantages for use in springs for special purposes. For example, they are nonmagnetic and have low electrical and thermal conductivity. They can be molded directly to dimensions without the development of any considerable internal stress. Their high corrosion resistance should make them of value for applications in chemical plants and installations subject to acid fumes or to salt air. Other applications may benefit from the strength-to-weight ratios of plastics, which are often higher than those obtained with spring-making metals. Also, the broad range of transparent and colored materials that can be used makes striking decorative effects possible.

The plastic springs are molded by drawing resin-soaked glass fibers through vinyl copolymer tubing and wrapping the loaded tubing in a helix around a mandrel. After curing in an air-circulating oven, the tubing is removed, leaving a solid plastic spring reinforced with glass fibers.

The most successful procedure uses vinyl chloride-vinyl acetate copolymer tubing having a $\frac{1}{4}$- or $\frac{3}{16}$-in. inside diameter and a $\frac{1}{8}$-in. wall thickness. Lengths of glass rovings are formed into a loose yarn, without twist, which is then doubled back to make a U-shaped bundle. This bundle is placed in a trough partly filled with liquid resin and is immersed until thoroughly soaked. A steel wire is threaded through the tubing attached to the bend in the U-shaped bundle, and used to pull the bundle through the tubing. Considerable force is applied to the wire by means of a small windlass.



The first step in making plastic springs is to soak a "rope" of glass fibers in a resin solution. A piece of piano wire is tied to one end of the rope and run through a section of vinyl copolymer tubing. The resin-soaked glass-fiber rope is drawn into the tubing and the excess resin solution is squeezed off.



The tubing is then wound around a mandrel to form a helix which is placed in an oven for curing. After curing, the plastic tubing is removed, leaving the finished spring.

When the tubing is completely filled, the wire is disconnected and the ends of the tubing sealed with hose clamps. The tubing is wound on a mandrel and the entire assembly is placed in an oven for curing under the conditions specified by the resin manufacturer. After removal of the tubing, post curing is performed as required, and the springs are cut and ground to the finished length.

Of the resins studied, the most promising were epoxides and polyesters. These resins are better suited for spring applications on the basis of torsional moduli, temperature sensitivity, and ease of handling. In general, the polyesters are more sensitive to elevated temperatures than the epoxy resins, but the epoxy materials vary widely in this respect.

Springs made from polyester resins with glass fiber reinforcement showed good energy recovery properties after short periods of storage at −40° F, but these properties were adversely affected by 13 days' exposure to 135° F while under stress. The best results were obtained with an epoxy resin cured with *m*-phenylenediamine. Springs made of this material had torsional moduli of rigidity of the order of 1.0×10^6 lb/in^2. In 2-in. lengths they deflected ½ in. under a static load of 25 lb. Three-inch springs of this type retained 40 percent of their original energy when compressed to their solid length and stored at 135° F for 13 days.

When the glass-epoxy springs were tested for recoverable energy a second time, higher values were invariably obtained. This characteristic "work tempering" of the epoxide resins was also demonstrated in torsion tests on nonreinforced plastic rods. An improvement of as much as 120 percent over the original available energy was indicated. This property of the material can be utilized by preloading the epoxide spring during storage or within 30 days before use.

The mechanical and thermal properties of the plastic springs can be varied widely by proper choice of materials and dimensions. For example, stiffer and probably more brittle springs result when the glass content is increased. At the same time, a high degree of homogeneity in static properties can be achieved. Under a load of 25 lb., 100 of the epoxy-resin springs had an average deflection of 0.53 in. with a standard deviation of 0.05 in.

[1] *For further details, see* Reinforced plastic springs, *by Frank W. Reinhart and Sanford B. Newman, Product Engineering (June 1956).*

In creep test of a plastic spring under load, spring deflection is measured on the dial indicator while the applied load is read from the dial in operator's hand.

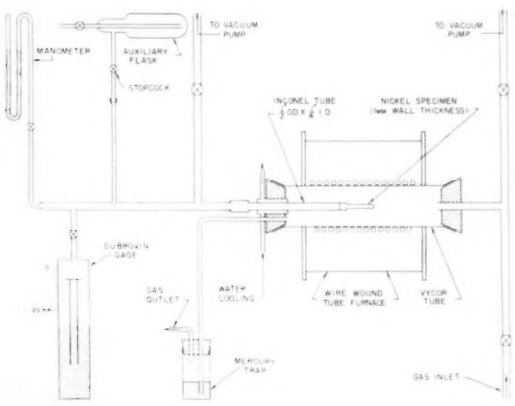
Diffusion of Hydrogen Through Ceramic Coatings

AN investigation of the diffusion rate of hydrogen through ceramic-coated nickel has recently been completed by J. R. Cuthill and R. W. Dixon of the enameled metals laboratory. The study, which was carried out as part of a larger program for the Wright Air Development Center, reveals that the ceramic reduces the hydrogen flow by a factor of about 20. The results indicate that it would be worthwhile to apply ceramic coatings to the metallic parts of high-temperature devices to minimize the diffusion of gases into an otherwise hermetically-sealed system.

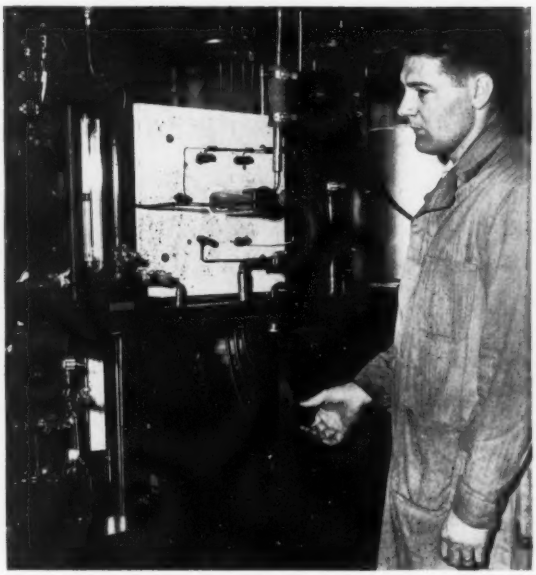
In an investigation of the creep rates of ceramic-coated metals at high temperatures, test specimens were exposed to various atmospheres, including hydrogen. Investigators have reported differences in the creep rates of bare metals in hydrogen and in air, and have attributed this difference to the oxide layer formed on the metal. An alternate explanation of the difference is that the metal absorbs some of the hydrogen, thus affecting the creep rate. Because the hydrogen diffusion through the ceramic coatings on the Bureau's specimens was unknown, tests were undertaken to measure the permeability of both coated and uncoated nickel to determine how much the ceramic inhibits the hydrogen flow.

High-purity nickel was chosen for the study because it is readily permeable to hydrogen at elevated temperatures. A tubular specimen of this material, closed at one end, was placed in a furnace; the open end of the tube was attached to an evacuated system. The system is equipped with pressure and volume measuring devices to determine the hydrogen diffusion rate through the specimen wall. The outside of the specimen is surrounded by hydrogen at about atmospheric pressure, and the furnace is heated to 1,400° F.

Three tests were made on the uncoated specimen, with hydrogen enveloping the outside of the tube while a vacuum was being drawn on the inside. The time when the vacuum pump was turned off was considered as the beginning of the test. In a supplementary test, the specimen was degassed. The experiment was started with vacuum on both the inside and outside of the tube, and hydrogen was let into the tube furnace. The result in this case was similar to that of the previous trials, except for an initial delay representing the time required for the hydrogen to permeate the specimen wall. The experiment was repeated with the same specimen coated with the NBS A–418 ceramic,[1] and the results were compared for both coated and uncoated specimens.



In apparatus for determining diffusion rate an evacuated system is attached to open end of a piece of nickel tubing. Tubing is placed in furnace containing hydrogen atmosphere. Pressure and volume measuring devices determine diffusion rate.



Studies with this equipment have shown that diffusion rate of hydrogen through nickel is reduced by a factor of about 20 if the metal is ceramic coated.

The diffusion tests established that the A–418 coating can reduce the diffusion rate through a specimen to at least 1/20 of the rate through the bare nickel, even though the coating is only about 1/40 as thick as the tubing wall. Good ceramic adherence to nickel is difficult to achieve. If a chromium-containing high-temperature alloy were to be used in such experiments, the improved adherence and coverage of the coating would be expected to yield even lower diffusion rates than obtained with coated nickel.

[1] Recent ceramic coatings for high-temperature alloys, *NBS Tech. News Bull.* **35**, 145 (October 1951).

Sensitive Calorimeter for Polymer Studies

A BUNSEN-TYPE calorimeter that measures precisely very small quantities of heat at room temperature has been devised by R. S. Jessup of the thermodynamics laboratory. Designed for investigating the basic thermodynamic properties of high polymers, this calorimeter[1] is particularly suited to measurement of heats of reaction, heats of solution, and heats of mixing of polymeric and other substances. It was developed in connection with a project to provide fundamental information on polymers, polymer solutions, and related materials of interest to the rubber industry.

The present calorimeter is similar in principle to previous Bunsen-type calorimeters, but it has been modified to permit the use of diphenyl ether instead of water as the calorimetric substance. In the original Bunsen ice calorimeter, designed in 1870, a heated sample was brought into thermal contact with an ice-water mixture in a closed system. Then the amount of ice melted by the sample in cooling to 0° C was determined from the weight of mercury drawn into the system to compensate for the volume decrease in the ice-water system. This apparatus as first devised was rather crude. However, in 1947 the Bureau developed an ice calorimeter,[2] based on the same principle, that gave very accurate results in determinations of high temperature specific heats and related thermodynamic data. Although the diphenyl ether calorimeter is similar in many respects to this latter ice calorimeter, it has been designed for a very different type of use.

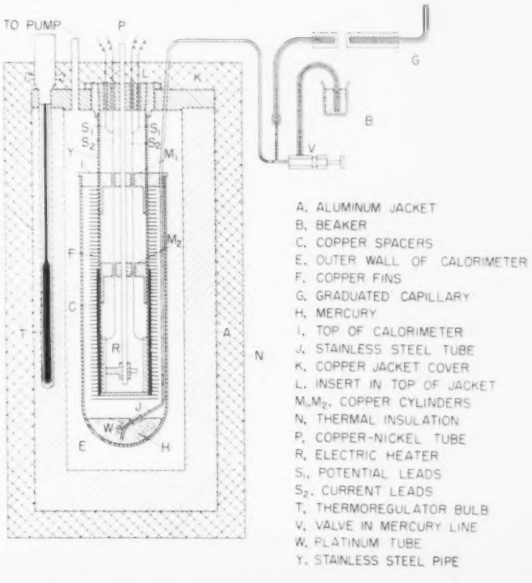
In measuring heats of mixing and solution, the use of diphenyl ether as a calorimetric substance has two important advantages. First, the relatively large volume changes of diphenyl ether on freezing and melting provide a sensitivity more than three times that of the ice calorimeter. Small quantities of heat can thus be measured with greater accuracy. Secondly, diphenyl ether melts at 26.87° C. This means that observations can be made at room temperature and the resulting data can be readily reduced to standard temperature at 25° C. Diphenyl ether has the further advantages of being quite stable and easily prepared in a state of high purity.

The diphenyl ether calorimeter consists essentially of a stainless steel cylindrical vessel (10 in. long, 3 in. in diameter) containing a central well designed to accommodate a reaction vessel. The calorimeter is enclosed in an insulating jacket, and the intervening space is evacuated. The central well, made of stainless steel pipe with a soldered brass bottom, extends upward through the brass top of the cylindrical vessel to an opening in the outer insulating jacket.

The space between the central well and the stainless steel calorimeter vessel is filled with purified diphenyl ether except for a pool of mercury in the bottom of the calorimeter. When the calorimeter is in use, the outer surface of the central well is covered with a mantle of solid diphenyl ether, which is in turn surrounded by liquid diphenyl ether. Heat transferred between the central well and the diphenyl ether causes partial melting or freezing, with a consequent change in the volume of the diphenyl ether and a flow of mercury into or out of the calorimeter through tubing that leads to an external mercury reservoir.

The quantity of heat is measured either by the volume or the weight of mercury thus transferred. If the volume of mercury is small, heat input is measured by the displacement of a mercury meniscus in a graduated glass capillary. If the mercury volume is large, heat input is determined from a combination of the change in weight of the mercury reservoir (a small beaker of mercury) and the change in position of the mercury meniscus.

Because the mercury capillary is horizontal, changes in the position of the mercury meniscus do not affect the pressure on the diphenyl ether in the calorimeter.



This Bunsen-type calorimeter measures very small quantities of heat in polymer studies. Calorimeter proper consists of stainless steel vessel (E) with brass top (I) through which passes the stainless steel pipe (Y) providing a central well. Space between the central well and the calorimeter vessel is filled with partially frozen diphenyl ether. Assembly composed of tube (P), electric heater (R), and copper cylinders (M_1 and M_2) is used only for calibration and is replaced by a reaction vessel during regular measurements. M_1 and M_2 provide zones of good thermal contact with well wall and thereby trap heat that would otherwise escape by conduction along leads or by radiation and convection. Copper fins (F) provide increased thermal contact between central well and diphenyl ether, while copper spacers (C) between lower fins promote uniformity in vertical distribution of heat transferred between well and diphenyl ether. Volume changes with freezing or melting of diphenyl ether cause a transfer of mercury between bottom of vessel and mercury measuring system at upper right. The calorimeter is suspended in an evacuated space within an aluminum jacket (A) surrounded by thermal insulation (N).

To reduce any possible effect of changes in barometric pressure on the position of the meniscus, the open end of the capillary is connected to a 1-liter flask immersed in oil in a Dewar flask. The pressure in the system is adjusted to atmospheric at the beginning of an experiment and remains practically constant during the time of an experiment. When only the mercury capillary is used to determine the volume of mercury moved, the mercury reservoir is closed off from the system by means of a needle valve.

To improve thermal contact between the central well and the diphenyl ether, copper fins are soldered to the outer wall of the well. These fins also serve to support the solid diphenyl ether, which is denser than the liquid. Copper spacers between the fins at the lower end of the well promote uniformity in the vertical distribution of heat transferred between the well and the diphenyl ether outside it.

An electric heater wound around the outside of the calorimeter is used to control the rate of freezing of the diphenyl ether before the beginning of an experiment. Too rapid freezing of the diphenyl ether causes entrapment of gaseous air. The freezing is carried out by bubbling air through water in the central well.

The insulating jacket is made of an aluminum cylinder with a copper cover and is surrounded by cork insulation. The jacket is maintained at the temperature of the calorimeter within ± 0.001 deg C by means of a thermoregulator. A 10-junction copper-constantan thermocouple measures the temperature difference between the top of the calorimeter and the jacket cover. Aluminum-foil radiation shields within the evacuated space between calorimeter and jacket aid in reducing thermal leakage from the calorimeter.

Once the calibration factor of a Bunsen-type calorimeter is known, the amount of heat energy added to the calorimeter can always be computed directly from observations on the mercury system. The diphenyl ether calorimeter was calibrated by electrical heating, using a 100-ohm electric heater in the central well in place of a reaction vessel. From the known electrical energy input and from observations of the mercury system, a calibration factor of 79.10 joules per gram of mercury was obtained. In 1947 Ginnings, Douglas, and Ball [2] obtained a value of 270.46 j/g of mercury for the ice calorimeter. The sensitivity of the diphenyl ether calorimeter is thus about 3.4 times that of the ice calorimeter. In general, the Bureau's studies show that the Bunsen-type diphenyl ether calorimeter can be used to measure quantities of heat of the order of 38 calories with a precision of about 0.05 percent.

[1] *For further details, see* A new Bunsen-type calorimeter, *by Ralph S. Jessup, J. Research NBS* **55,** *317 (1955) RP2636.*

[2] Improved ice calorimeter in high-temperature research, *NBS Tech. News Bull.* **31,** *63 (June 1947). See also* An improved ice calorimeter—the determination of its calibration factor and the density of ice at 0° C, *by Defoe C. Ginnings and Robert J. Corruccini, J. Research NBS* **38,** *583 (1947) RP1796.*

Electromotive Series for Solid and Molten Chlorides

AN electromotive-force series for solid and molten chlorides has been developed that is based on thermodynamic calculations using the electronic computer, SEAC. The series [1] gives theoretical electromotive forces for galvanic cells containing 96 different solid and molten chloride electrolytes. When listed in order of magnitude, the computed emf's provide a relative scale of chemical activity that should prove helpful to scientists and engineers working out new processes in high-temperature chemistry.

The necessary calculations and theoretical analyses for the chloride series were carried out by W. J. Hamer, M. S. Malmberg, and Bernard Rubin of the electrochemistry laboratory. Their results represent the first step in a long-range program for the development of an electromotive series of the metallic elements in nonaqueous, fused, or molten systems.

The electromotive series found in chemistry textbooks lists the metals in the order of the amount of emf set up between metal and solution when the metal is placed in an aqueous solution of any of its salts at unit activity. Chemists have long used this series to determine which of two metals will displace the other from an electrolytic solution. With the increasing emphasis on high-temperature processes in atomic energy and other fields, a need has arisen for an analogous series of the metals in molten or fused systems.

The chloride series that has been developed represents the sum of the metallic and chloride potentials; it is thus of less general utility than a series for the individual metallic elements. However, it should still prove useful in such high-temperature fields as ceramics, electrowinning, and thermal batteries. Additional electromotive series for other salts, such as the bromides and fluorides, must first be calculated before the potentials of the individual metals can be isolated.

The Bureau's study provides data over a wide range of temperatures on the theoretical electromotive forces for the various chloride electrolytes. Radium chloride has the highest potential while auric chloride is at the other end of the list. Relative position in the series corresponds to reducing power. Thus, if radium were placed in fused auric chloride, it would reduce the auric ion to metallic gold.

The study also showed that the emf's for aqueous and solid chlorides differ by amounts related to the free energy of dilution of saturated aqueous solutions of the chlorides. For highly soluble salts, the emf for aqueous systems is higher than for molten systems; for sparingly soluble salts the reverse is true.

[1] *For further details, see* Theoretical electromotive forces for cells containing a single solid or molten chloride electrolyte, *by Walter J. Hamer, Marjorie S. Malmberg, and Bernard Rubin, J. Electrochem. Soc.* **103,** *8 (1956).*

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